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ARTICLE

Dihydroxyacetone conversion into lactic acid in aqueous media in the presence of metal salts: influence of the ionic thermodynamic equilibrium on the reaction performances

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The catalytic conversion of dihydroxyacetone (DHA) to lactic acid (LA) via pyruvaldehyde (PA) in aqueous media was studied using different homogeneous metal salts. A kinetic model was developed and the parameters corresponding to each reaction steps were estimated. Agreement between experiments and simulated results was excellent and the performance of the different catalysts was consistent with previous studies described in the literature. Aluminium salts, which show the best performance, were tested in a whole range of concentrations and at different pH, in order to identify the catalytically active ionic species. It was confirmed that the DHA to pyruvaldehyde (PA) dehydration step is catalyzed by both Brønsted and Lewis acids whereas the consecutive reaction of PA to LA is solely catalyzed by Lewis acids. Moreover, comparing thermodynamic analysis of the reaction media and kinetic parameters demonstrated that cationic hydroxyl-aluminium complexes $[Al(OH)_h]^{(3-h)+}$ formed in situ by the hydrolysis of the aluminium aqua complexes like $[Al(OH_2)_6]^{3+}$ are the most active Lewis acids.

Introduction

With declining petroleum reserves as well as environmental concern for sustainable chemistry, a growing interest in the production of chemicals from renewable biomass has emerged.[1] Among these chemicals, lactic acid (LA) has been identified as a potentially interesting molecule. Not only can it be synthesized from bio-based feedstocks[2,3] but it also has numerous applications in different industries[4] (food, cosmetic, biodegradable polymers). Stereopure L-LA is currently produced by fermentation of carbohydrates. However, this process necessitates complex separation steps[4] and generates large amounts of unvaluable gypsum ($CaSO_4$). Hence, a lot of work has been focused recently on finding a more efficient chemical catalytic synthesis route, often leading to racemic LA, giving priority to water as an inexpensive and environmentally benign solvent.[2]

A few studies reported in the literature[5,6] involve the use of homogeneous catalysts in hydrothermal conditions to selectively convert cellulosic feedstocks into LA via hexoses as key intermediates. It is generally reported that fructose, supplied by glucose isomerization, undergoes a retroaldol reaction to trioses dihydroxyacetone (DHA) and glyceraldehyde (GLY), which opens the way to LA as final stable product. DHA and GLY constitute reactive intermediates and their conversion to LA with high selectivities remains a challenge. In this present study, we will therefore focus on the final step of the reaction, i.e. the catalytic conversion of DHA into LA. Several homogeneous catalysts such as metal salts[7,8] or heterogeneous catalysts such as zeolites[9–11] and tin phosphates[9,10] were proposed.

It is well admitted that this reaction proceeds in two steps:[5,8,9,11–20] (i) DHA is first converted into pyruvaldehyde (PA) by successive keto-enol tautomerization and dehydration;[8,9,16,18] this reaction is described to be catalyzed by both Lewis and Brønsted acids.[8,11,18] (ii) Rehydratation of PA followed by a 1,2-hydride shift yields LA; for this second step, Lewis acids are believed to lead to higher catalytic performances than Brønsted acids.[8,18,21] It has to be noted that in water, PA exists mainly in two forms: hydrated (56%) and di-hydrated (44%). Since the different

Obviously, the rate-limiting step depends strongly on the nature of the catalyst acid sites. Wang et al.[9,10] showed that the conversion of PA to LA was the limiting step over tin phosphate catalysts, whereas West et al.[20] found the opposite result over H-USY zeolites.

During the course of the reaction, brown soluble and insoluble products are formed, both with homogeneous[8,18] and heterogeneous[10,13,22–24] catalysts. These unwanted products that are attributed to either DHA or PA oligomers can lead to a drastic reduction of the LA yield and deactivation of catalysts.

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Regarding their capacity to produce LA with a very high yield in water, previous studies have shown that aluminium and chromium salts were very promising homogeneous Lewis acid catalysts. Using different Cr and Al salts at 140°C, Rasrendra et al.[8] obtained selectivity to LA in the range 80-90% at total conversion of DHA. A small effect of the nature of the anion was observed, with LA yields varying in the order $Cl^- \approx NO_3^- > SO_4^{2-}$. Lux et al.[18] obtained a 77% yield of LA at 97% DHA conversion using aluminium sulphate at 99°C. The unique performance of Al^{3+} and Cr^{3+} (compared to all the other metal tested) are not explained at the moment. Interestingly, Lux et al.[18] also observed that the rate constant of the second step of the reaction (conversion of PA to LA) varied non-linearly with the catalyst concentration, without providing any explanation.

In that respect, the study by Choudhary et al.[25] on the $CrCl_3$-catalyzed transformation of glucose to fructose to yield 5-HMF in aqueous media might provide useful indications. Indeed, some parallels can be drawn between glucose-fructose and GLY-DHA / PA-LA isomerization as they may involve similar active species for the aldose-ketose isomerization. By using the commercial OLI Systems software (OLI Systems Stream Analyzer Software, OLI Systems, 2012), the concentrations of the different cations generated from the dissolution of $CrCl_3$ in water were evaluated by the authors. Comparison of the glucose initial conversion rates with the concentrations of the different cations indicated that the pentahydrated $[CrOH]^{2+}$ cation, although less concentrated than $[Cr]^{3+}$ in the aqueous phase, was the most active Cr species for glucose isomerization, thanks to strong interaction of glucose in the Cr first coordination sphere.

Following the methodology proposed by Choudhary et al.[25], the aim of this study is to identify the most catalytically active species of the Al salts solutions - which are among the most efficient homogeneous catalysts for this reaction - for the two reaction steps involved in the DHA to LA conversion. This information is essential in order to – ultimately - optimize the reaction conditions and the catalytic systems. To do so, the following strategy was applied. First, a kinetic model was developed and its reliability was tested by simulating the concentration profiles over time for different metal salts, assumed to provide Brønsted and Lewis acid species in the aqueous phase and leading to very different catalytic performances. Influence of a pure Brønsted acid on the kinetics was also evaluated with H_2SO_4. The experiments were conducted at relatively low temperature (≈90°C) so as to slow down the reactions and evaluate the kinetic parameters as accurately as possible. Once the model was validated, the kinetic parameters for aluminium salts were evaluated on a large range of concentrations and with different counter anions. The effect of addition of H_2SO_4 in the catalytic solution was also tested. To identify the most catalytically active cations for each reaction step, the kinetic parameters were finally compared with the aqueous phase aluminium cations concentrations as simulated by the OLI software.

Experimental

Materials

1,3-dihydroxyacetone dimer (DHA, >97%), pyruvaldehyde (PA, >90%), glyceraldehyde (GLY, >90%), $Al_2(SO_4)_3 \cdot 18H_2O$ (>95%) and $ErCl_3$ (99.9%) were purchased from Sigma-Aldrich. L-lactic acid (LA, >98%) was purchased from Alfa Aesar, while $ZnSO_4 \cdot 7H_2O$ (>99.5%) was purchased from Fluka, and H_2SO_4 (95-97%) from Merck. All products were used as received.

Kinetic data measurements

The reactions were conducted in a 250 mL three-neck round-bottom flask placed in a temperature controlled oil bath. The flask was equipped with a water condenser, a temperature sensor and a rubber septum. Agitation was performed with a magnetic stirrer. All reactions were conducted under ambient atmosphere and pressure. Deionized water (200 mL) and the catalyst were introduced in the flask. When the temperature of the suspension was stabilized, DHA was injected at time t=0. Samples were withdrawn with a 1 mL syringe through the septum. The amount of products were quantified by using high-performance liquid chromatography (HPLC Shimadzu Prominence system equipped with a RI differential refractometer detector and a ICSep COREGEL 107H column). Oligomers were quantified via the carbon molar balance which was compared to the initial DHA molar concentration (i.e. all the unknown species are assumed to be oligomers).

Experiments conducted without any catalyst yielded a 6% and 2% conversion (defined as the molar percentage of DHA converted) after 400 min at 90°C and 80°C, respectively. The thermal conversion of DHA was therefore thereafter neglected. No deactivation of the catalysts (e.g. by precipitation) was observed during the experiments.

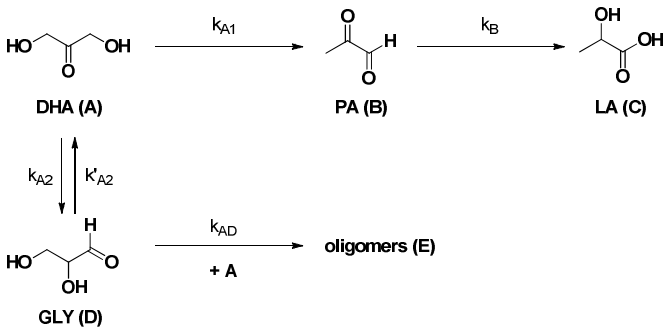
The pH values of the solutions were measured using a Metrohm 744 pH meter.

Kinetic model

The mechanism proposed for the conversion of DHA into LA is presented on Scheme 1. Even though both the conversion of DHA to PA and the conversion of PA to LA comprise different steps (i.e. PA has to be monohydrated before it can undergo a hydride shift), they have been considered as elementary steps and represented by a single kinetic parameter, as done in other literature kinetic studies[8,18].

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Scheme 1: Proposed reaction mechanism for the conversion of DHA into LA *via* PA

For a kinetic modeling of DHA conversion to LA, the impact of DHA isomerization to glyceraldehyde (GLY) has to be taken into account. Different studies in the literature[8–10,20] compare batch concentration profiles when DHA or GLY are used as the starting material and all lead to the same conclusions: GLY isomerizes to DHA very quickly, the direct conversion of GLY to PA being negligible. Moreover, Liang et al.[26] reported experimental and calculated free enthalpies of reaction in the range of 2.3 to 10.9 kJ/mol for isomerization of DHA to GLY, confirming that the conversion of DHA to GLY is thermodynamically unfavourable. In the present study, non-negligible GLY concentrations were measured in some experimental conditions probably thanks to the mild reaction conditions. The thermodynamic equilibrium between DHA and GLY was therefore accounted for in addition to the main consecutive reactions DHA→PA→LA. Furthermore, the model included the involvement of GLY in the formation of the brown insoluble oligomers. A more complex model, that included DHA and PA oligomerization was also implemented (see S.I.), but the best fit of the experimental points was obtained with the scheme proposed in Scheme 1 with only the oligomerization reaction from GLY. This scheme was therefore used for the subsequent stages of this study.

Supposing that all the reaction steps are elementary steps, the following set of differential reactions is obtained for the concentrations of the species:

$$\frac{dA}{dt} = -k_{A1} \cdot A - k_{A2} \cdot A + \frac{k_{A2}}{K_{AD}} \cdot D - k_{AD} \cdot AD \quad (1)$$

$$\frac{dB}{dt} = k_{A1} \cdot A - k_B \cdot B \quad (2)$$

$$\frac{dC}{dt} = k_B \cdot B \quad (3)$$

$$\frac{dD}{dt} = k_{A2} \cdot A - \frac{k_{A2}}{K_{AD}} \cdot D - k_{AD} \cdot AD \quad (4)$$

$$\frac{dE}{dt} = k_{AD} \cdot AD \quad (5)$$

where K_{AD} is the thermodynamic equilibrium constant :

$$K_{AD} = \frac{k_{A2}}{k'_{A2}} \quad (6)$$

Equations (1) to (5) were numerically solved with the SCILAB software using the *ode* function. Function *optim* was used for the parameters estimation, the objective function being the least square difference between the experimental and simulated concentrations.

Results and discussion

Comparison of different metal salts and sulphuric acid

DHA and products concentrations profiles as a function of reaction time for the different salts were measured under the same experimental conditions at 90°C (see Table 1). The concentration profiles are displayed on Fig. 1. It is noteworthy that due to oligomerization reactions, the total concentration of products in solution (expressed in mol/L) drops during the course of the reaction.

The simulated and experimental concentrations are in very good agreement, which means that the reaction mechanism proposed in is valid for all the tested salts. Moreover, the concentration profiles are consistent with literature results involving the same catalysts for DHA conversion to LA.[8,15,17,18,20,22]

Indeed, H_2SO_4 is very selective towards the formation of the intermediate PA, meaning that Brønsted acids are active neither for the conversion of PA into LA nor for the DHA to GLY isomerization. The absence of oligomers is consistent with the reaction scheme proposed on Scheme 1: the condensation with DHA cannot take place in the absence of GLY.

Furthermore, aluminium sulphate is by far the most selective catalyst to LA. In that case, PA and GLY appear as intermediates and the amount of oligomers formed is very low.

By contrast, $ErCl_3$ and $ZnSO_4$ display similar poor performances: at the end of the experiment, PA and oligomers are the main products. The outstanding performances of $ErCl_3$ for the hydrothermal conversion of cellulose to lactic acid described by Lei et al.[6] are not found here. This may be explained by the huge gap of temperature (240°C for Lei et al.[6] vs. 90°C in this work).

The resulting kinetic parameters are gathered in Table 1. For $Al_2(SO_4)_3$ and H_2SO_4, the k_{A1} parameter is in the same order of magnitude. Aluminium salts can generate both Lewis acidity from cationic aqua complexes like $[Al(OH_2)_6]^{3+}$ and Brønsted acidity resulting from the hydrolysis of the latter into mono- or polyhydroxyl complexes $[Al(OH_2)_n(OH)_h]^{(3-h)+}$, see eq. (7) and (8). In order to discriminate these two effects, complementary experiments were performed.

First, the proton concentration of the aluminium sulphate aqueous solution [0.09 M] was evaluated via pH measurements at 90°C. A pH value of 2.81 was measured, i.e. a $[H_3O^+]$ concentration ≈ 1.5 10^{-3} M. Then, from experiments performed at different concentrations of H_2SO_4, the linear relationship between k_{A1} and the H_3O^+ concentration was established, as shown by Fig. 2.

	Experimental conditions			
Salts conc. (M)	0.09 ± 0.005			
Temperature (°C)	87 to 93			
DHA initial conc. (M)	0.09 ± 0.005			
	Estimated parameters (estimated relative standard error %)			
catalyst	H_2SO_4	$Al_2(SO_4)_3$	$ErCl_3$	$ZnSO_4$
k_{A1} (s^{-1})	8.45 10^{-5} (±3%)	1.03 10^{-4} (±0.9%)	2.06 10^{-5} (±1.9%)	1.36 10^{-5} (±4.1%)
k_B (s^{-1})	0	2.03 10^{-4} (±1.8%)	2.88 10^{-5} (±5.5%)	2.71 10^{-5} (±9.8%)
k_{A2} (s^{-1})	0	3.36 10^{-5} (±16.7%)	4.70 10^{-5} (±16.1%)	5.24 10^{-5} (±14.5%)
k_{AD} (M^{-1} s^{-1})	0	6.99 10^{-4} (±15.4%)	1.91 10^{-3} (±6.1%)	5.23 10^{-3} (±6.8%)
K_{AD} (-)	-	0.108 (±9.2%)	0.116 (±8.4%)	0.140 (±10%)
k_B/k_{A1}	0	1.97	1.4	1.98
Degree of explanation (%)	99.7	99.8	97.9	99.8

Table 1: experimental conditions and corresponding parameters for different salts

The proton contribution to the $Al_2(SO_4)_3$ kinetic parameter was finally estimated from these data: k_{A1} = 1.18 10^{-6} s^{-1}, i.e. approx. 1% of the overall value. The high value of k_{A1} obtained with aluminium sulphate is therefore solely induced by its Lewis acidity or might result from a synergy effect between Lewis and Brønsted sites.

The kinetic parameters for aluminium sulphate (Table 1) are nearly an order of magnitude higher than those determined for the other Lewis acids. Only the parameter related to DHA isomerization to GLY (k_{A2}) is close to that for other salts. Hence, $Al_2(SO_4)_3$ strongly promotes the DHA conversion to PA (and then to LA), but it does not favour the parallel path leading to oligomers via GLY. As expected, the thermodynamic parameter K_{AD} is nearly constant (given the experimental uncertainties) for all salts and gives a free enthalpy of reaction around 6 kJ/mol, in agreement with results reported in the literature for keto-enol tautomerization between DHA and GLY (2.3 to 10.9 kJ/mol).[26]

The activation energies were also evaluated for aluminium sulphate and sulfuric acid (see S.I.). Comparable values (respectively 98 kJ/mol and 92 kJ/mol) were found for reaction A1 (DHA to PA conversion). The aluminium sulphate activation energy for reaction B (PA to LA conversion) is 82 kJ/mol, i.e. nearly 16 kJ/mol smaller than that of reaction A1, highlighting the ability of aqueous phase aluminium species to specifically activate the pyruvaldehyde molecule.

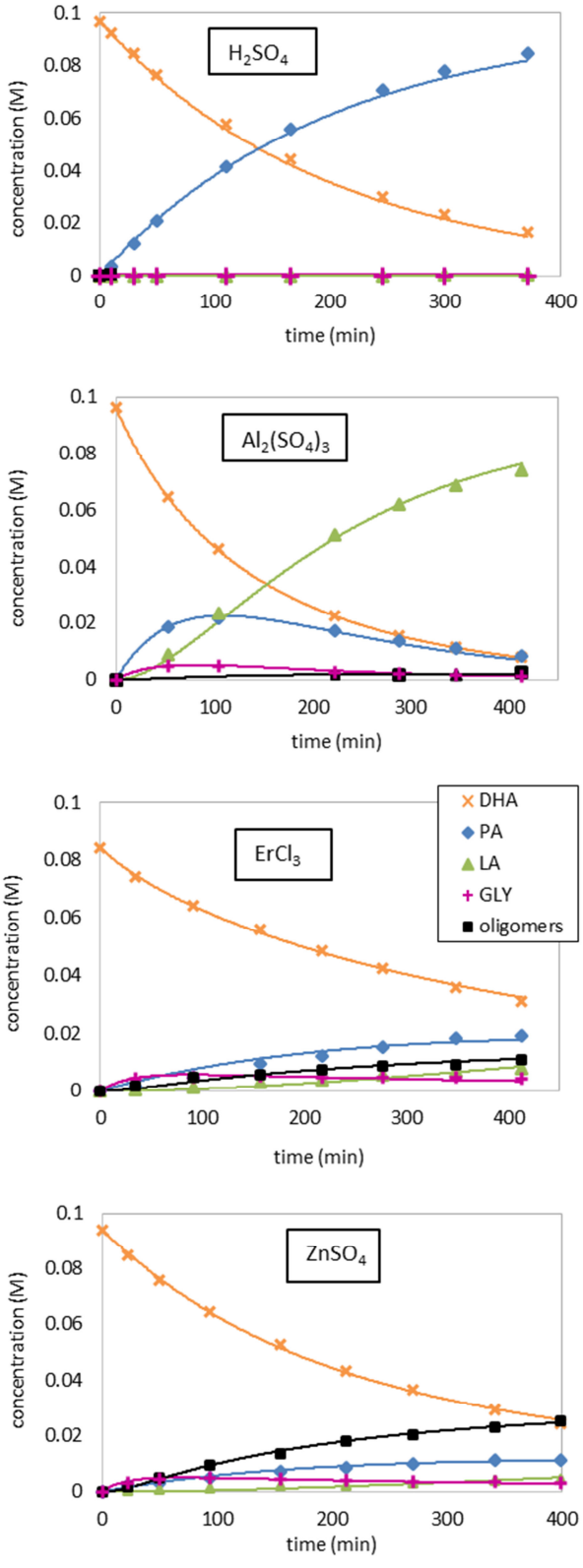


Figure 1: Concentrations profiles as a function of time in the presence of H_2SO_4 and the different metal salts for the experimental conditions and kinetic parameters specified in Table 1 (points correspond to experiments; lines represent model predictions)

Aluminium salts

In order to identify the catalytically active species, it is necessary to consider which aqueous species of aluminium is most likely to be present in the studied solutions. Over the years, numerous studies have been dedicated to the complex behaviour of aluminium ions in aqueous solution, using either

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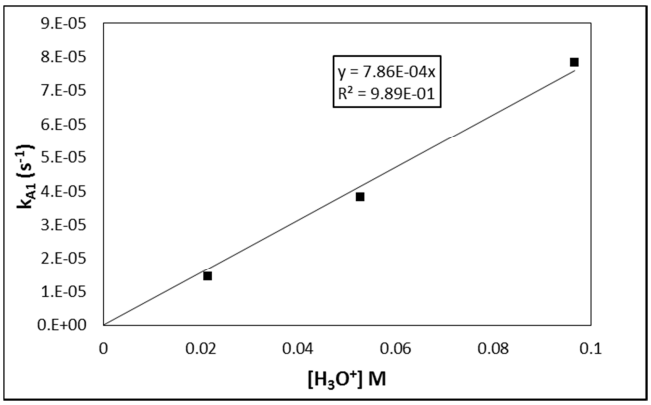


Figure 2: : Evolution of k_{A1} kinetic parameter as a function of proton concentration (90°C, addition of H_2SO_4).

analytical methods (X-Ray,[27] Raman,[28,29] NMR[30] spectroscopy, mass spectrometry[31,32]), macroscopic thermodynamic properties[30,33] and DFT simulations[27,29,32,34,35]. Although a great variety of chemical species have been identified, including polymeric Al complexes,[31,32] it is generally admitted that under acidic conditions, the predominant aluminium species are the aqua complex formed by interaction of the Al^{3+} cation with water molecules (Eq 7), the hydroxyl complexes resulting from water hydrolysis (Eq 8), and other complexes formed with anionic species potentially present in the aqueous solution (Eq 9).

It is well known that dissolved aluminium is essentially in the form of a cationic aqua complex with 6 water molecules, when pH is below neutrality[27,29,34] :

$$Al^{3+} + 6H_2O \rightarrow [Al(OH_2)_6]^{3+} \quad (7)$$

Hydroxides or other anions (such as sulphate) can displace water molecules to form additional complexes, following different equilibrium reactions (for clarity, water molecules are not included in the formula of the complexes thereafter).

Hydrolysis of aqua complexes takes place according to the following reaction, with a loss of proton[33,34,36,37]:

$$[Al^{3+}] + 2h \cdot H_2O \Leftrightarrow [Al(OH)_h]^{(3-h)+} + h \cdot H_3O^+ \quad (8)$$

Under acidic conditions (pH < 5), only $[Al(OH)]^{2+}$and $[Al(OH)_2]^+$ are present in significant concentrations in solution.[34,36,37]

In the presence of the sulphate anion, the formation of sulphato complexes has been demonstrated[28,30]:

$$[Al^{3+}] + p \cdot {SO_4}^{2-} \Leftrightarrow \left[Al(SO_4)_p\right]^{(3-2p)+} \quad (9)$$

On the contrary, the nitrate and chloride anions are much less inclined to form thermodynamically stable complexes with aluminium in aqueous solutions.[29,31]

Also, in acidic conditions, the equilibrium between the sulphate and hydrogen sulphate anions has to be taken into account:

$$H_3O^+ + {SO_4}^{2-} \Leftrightarrow HSO_4^- + H_2O \quad (10)$$

Equations (8) to (10) are governed by their equilibrium constant, i.e. depend on the activity of each ionic species. From equation (8), it is clear that when aluminium salts are dissolved into water (with no addition of Brønsted acids), the concentration of $[Al(OH)_h]^{(3-h)+}$ cations will be inversely proportional to the pH of the aqueous solution. Reversely, addition of protons to the solution will reduce the concentration of the hydroxyl complexes.

Kinetic experiments were performed with solutions containing 0-0.1 M aluminium salt. The evolution of the kinetic parameters as a function of $Al_2(SO_4)_3$ concentration are displayed on Fig. 3a.

In theory, the kinetic parameters should vary linearly with the catalyst concentration.

Two different trends could be observed: the evolution of k_{A1} is linear, whereas k_B and k_{A2} vary non-linearly as a function of $Al_2(SO_4)_3$ concentration. The confidence in these results is supported by the excellent agreement with the values obtained by Lux et al.[18] at 99°C (Fig. 3b). Presumably, the different reactions are not catalyzed by the same ionic species: the DHA to PA dehydration reaction is catalyzed by a cation whose concentration is proportional to the amount of $Al_2(SO_4)_3$ introduced in solution whereas both the conversion of PA to LA and the DHA isomerization to GLY are catalyzed by another complex cation, whose relative concentration drops as $Al_2(SO_4)_3$ concentration increases.

In order to identify the nature of these species, the influence of pH was studied. Experiments were carried out with a constant concentration of $Al_2(SO_4)_3$ (0.09 +/- 0.005 M) and addition of various concentrations of H_2SO_4. The effect of H_2SO_4 addition on the kinetic rate constants is shown in Fig. 4. The addition of the inorganic acid into the reaction medium gives a rapid decrease of k_B, k_{A2} and k_{AD} i.e. the reactions that are presumably catalyzed by Lewis acidity. The formation of the ionic species active for these two reactions is therefore hindered at higher pH.

As shown by eq. (8), this should be the case when aqua complexes hydrolyze into hydroxyl complexes, which seems to indicate that the $[Al(OH)_h]^{(3-h)+}$ cations are the most active Lewis catalytic species in solution.

The effect of sulphuric acid on kinetic constant k_{A1} is less clear: there is a small decrease of k_{A1} upon addition of 0.02 M H_2SO_4, but an inverse tendency is observed for higher concentrations. Since this reaction is catalyzed both by Lewis and Brønsted acidity, precise knowledge of the nature and repartition of each Al cation species present in the reaction medium is needed to interpret these results.

To do so, the concentrations of the different Al cations were calculated using the OLI software.

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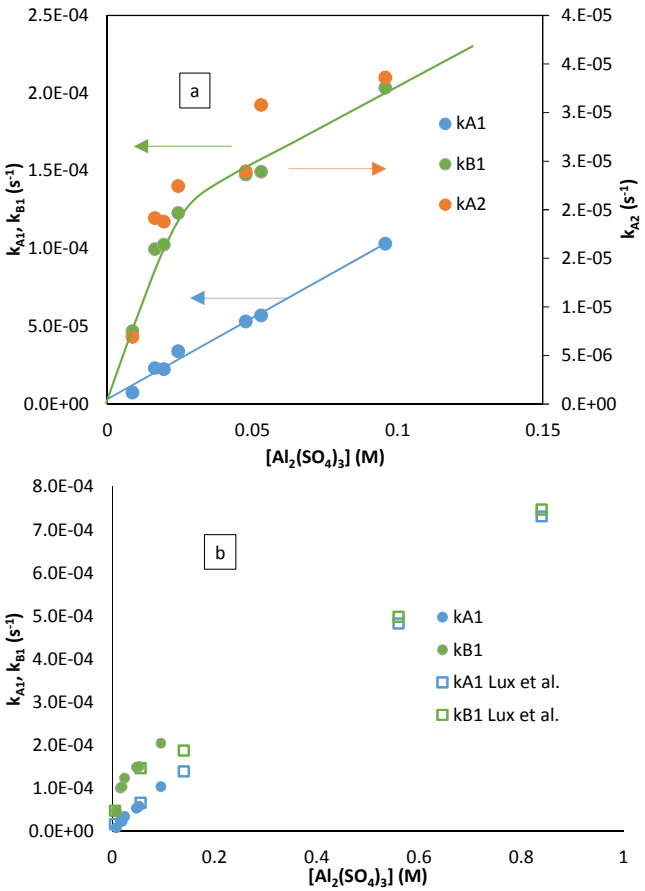
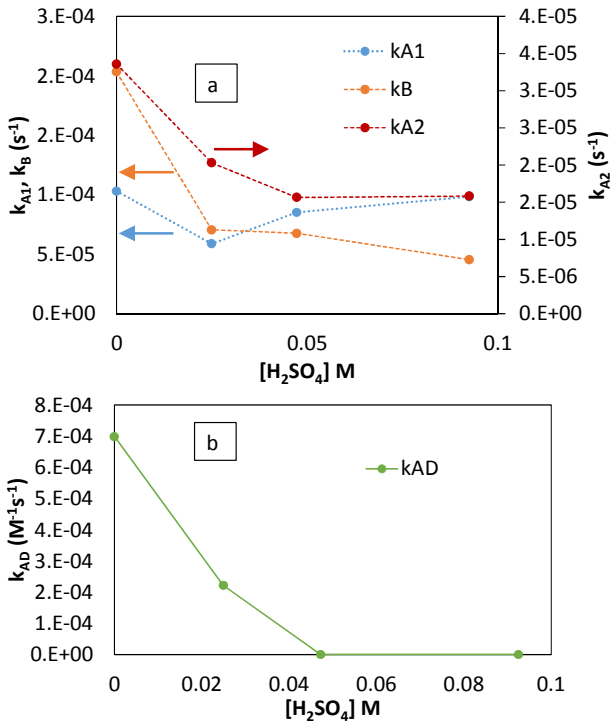


Figure 3: Evolution of the kinetic parameters with $Al_2(SO_4)_3$ concentration (a: this work at 90°C, lines are guide for the eyes ; b: comparison with Lux et al. (T=99°C)

So as to test the accuracy of the simulator, the pH of aqueous solutions of $Al_2(SO_4)_3$ were measured at different concentrations and temperatures and compared to the values calculated by OLI (Fig. 5). The predicted concentrations differ significantly from the experimental ones in the whole range of

Figure 4: Influence of pH on the kinetic parameters for $Al_2(SO_4)_3$ aqueous solutions of 0.09 +/- 0.005 M



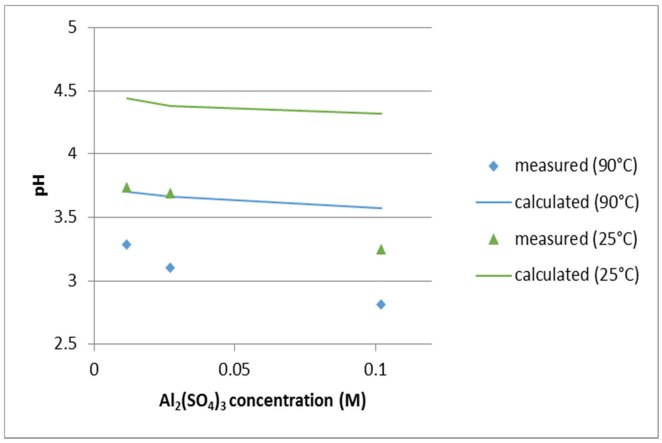


Figure 5: Influence of pH on the kinetic parameters for $Al_2(SO_4)_3$ aqueous solutions of 0.09 +/- 0.05 M)

concentrations. Around 0.1 M $Al_2(SO_4)_3$, the experimental and calculated pH differ by nearly one unity, that is to say the concentration of H_3O^+ is underestimated by a factor of 10.

It is therefore clear that the simulations cannot be used to quantitatively interpret our results. Still, useful information can be extracted from the tendencies predicted by the model, and the calculations were thus carried out for the experimental conditions of Fig. 4. The results, shown on Fig. 6, confirm our prior analyses. The calculations predict that the addition of H_2SO_4 leads to higher concentrations of H_3O^+, $[Al^{3+}]$ and $[AlSO_4]^+$, whereas both the concentrations of $[AlOH]^{2+}$ and $[Al(OH)_2]^+$ drop. Comparing Fig. 4 and Fig. 6 allows to reach the following conclusions:

1. Only the hydroxyl-aluminium complexes $[AlOH]^{2+}$ and $[Al(OH)_2]^+$ can possibly catalyze reactions B and A2, i.e. the PA to LA and DHA to GLY isomerization steps. The same conclusion – a strong Lewis acidity of the hydroxide complexes – has been reached by Choudhary et al.[25] for the glucose to fructose isomerization by $[CrOH]^{2+}$ chromium ion in solution. The mechanism proposed by the authors – complex formation between two adjacent oxygen groups and the metallic center, followed by hydride transfer from the C2 to C1 carbon and back proton transfer to O1 – can be applied to the (hydrated) PA to LA and DHA to GLY isomerization steps. The fact that the kinetic parameters corresponding to these two reactions – k_B and k_{A2} – follow the same evolutions as a function of $Al_2(SO_4)_3$ concentration (Fig. 3) and when H_2SO_4 is added to the aqueous solution (Fig. 4) confirm this hypothesis.
2. Reaction A1 is probably catalyzed both by hydroxyl-aluminium complexes (explaining the lower value of k_{A1} when adding 0.02 M of H_2SO_4) and by either $[Al^{3+}]$ and/or H_3O^+ (leading to an increase of k_{A1} for higher H_2SO_4 concentration). To evaluate more precisely the contributions of $[Al^{3+}]$ and H_3O^+ a more accurate thermodynamic model would be needed.

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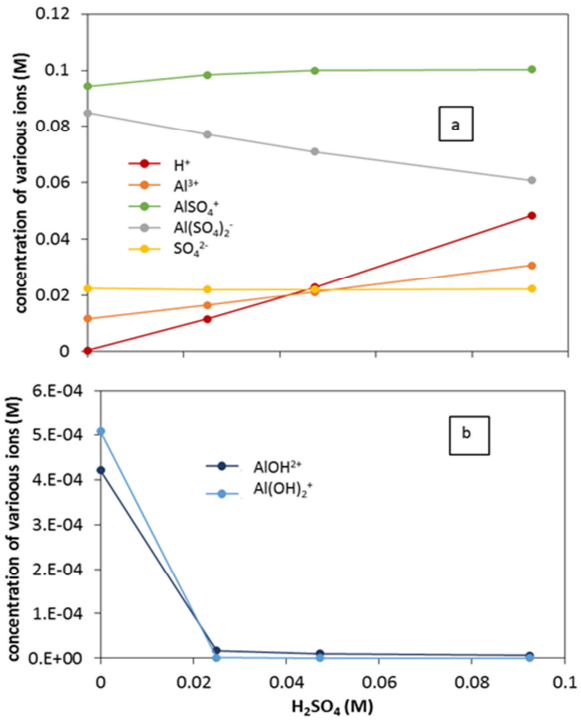


Figure 6: Evolution of the concentration of the different Al cations as a function of H2SO4 concentration calculated using the OLI software (T=90°C, $Al_2(SO_4)_3$ =0.09 M) (a: H+, Al^{3+} and $AlSO^{4+}$; b: $Al(OH)^{2+}$ and $Al(OH)_2^{+}$)

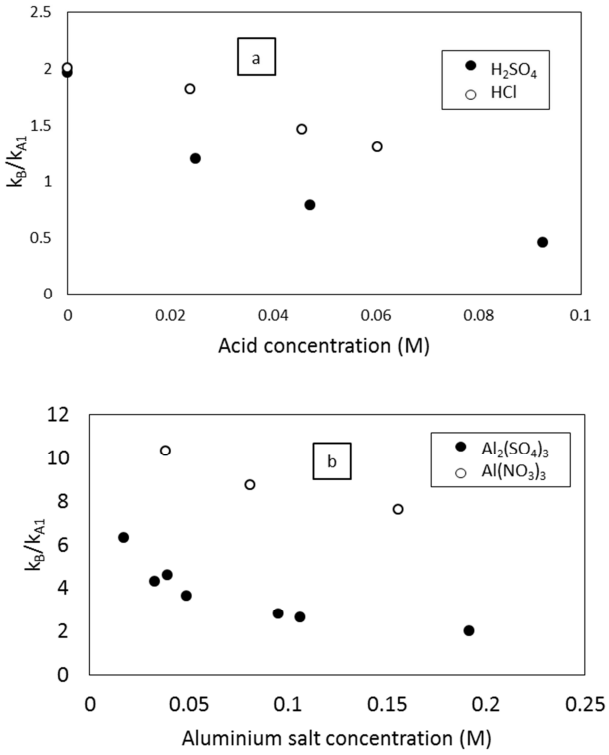


Figure 7: Rate limiting step for the conversion of DHA to LA at T=90°C (a: effect of the addition of acids at $Al_2(SO_4)_3$=0.09 M ; b: effect of the concentration of different aluminium salts)

From this analysis, it is also possible to conclude that the Lewis acid ionic species that catalyze reaction A1 in the absence of strong acid (cf. Fig.3) are very probably the aqua and hydroxyl complexes of Al^{3+}.

Since the conversion of DHA to LA is the result of two successive reactions that are catalyzed by different cationic species, the rate limiting step is strongly dependent on the nature and concentration of the catalyst.

The effect of the counter anion on the rate limiting step is illustrated on Fig. 7. The global tendencies are not affected by the nature of the counter anion: both the addition of a strong acid and increasing concentration of aluminium salts result in a decrease of the k_B/k_{A1} ratio. However, the introduction in the reaction medium of different anions changes the absolute values of this ratio. For less complexing anions[29,31,32] such as Cl^- and NO_3^-, the kinetic of the second reaction step step k_B is promoted. This may be ascribed to the less favorable formation of aluminium nitrate and aluminium chloride complexes, resulting in higher concentrations in hydroxyl-aluminium complexes.

Conclusions

Different homogeneous catalysts have been tested for the conversion of DHA to LA and a kinetic model has been developed, which enables a very satisfactory representation of the experimental concentration profiles for all catalysts.

In agreement with previous studies, the aluminium salts are identified as very efficient catalysts for this reaction, with a selectivity to LA of over 80% at 90% conversion of DHA.

An attempt was made to simulate the ionic equilibrium concentrations in the reaction medium using the commercial software OLI. Discrepancies between calculated and measured pH values of different $Al_2(SO_4)_3$ solutions lead us to the conclusion that the model, although useful to predict general tendencies, is not sufficiently accurate to quantitatively interpret the present results. In order to optimize the formulation of the catalytic system, disposing of reliable thermodynamic models would be needed. Moreover, given the concentrations needed in industrial processes, the models have to be valid for very high ionic strengths, i.e. in strongly non ideal thermodynamic conditions.

Nonetheless, a qualitative analysis of the evolution of the different kinetic parameters at different $Al_2(SO_4)_3$ concentrations and for $Al_2(SO_4)_3/H_2SO_4$ mixtures, showed that the two successive reactions (DHA to PA and PA to LA) are catalyzed by different ionic species:

1. the dehydration of DHA to LA is catalyzed by Brønsted acidity, and also very probably by $[Al(OH_2)_6]^{3+}$,
2. the further conversion of LA to PA is catalyzed by the hydroxyl-aluminium $[Al(OH)_h]^{(3-h)+}$complexes formed by hydrolysis of aqua complexes.

These results were confirmed by complementary experiments with different counter-anions. For less complexing anions, which generate more hydroxyl-aluminium complexes in solution, the first reaction step is even more limiting.

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